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METHODS OF TEST FOR SYNTHETIC RUBBER

PART 1 DETERMINATION OF ANTIOXIDANTS

[SR : 1]

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Indian Standard

METHODS OF TEST FOR SYNTHETIC RUBBER

PART 1 DETERMINATION OF ANTIOXIDANTS

[SR : 1]

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(*Continued on page* 10)

Indian Standard

METHODS OF TEST FOR SYNTHETIC RUBBER

PART 1 DETERMINATION OF ANTIOXIDANTS

[SR : 1]

0. FOREWORD

0.1 This Indian Standard was adopted by the Indian Standards Institution on 28 March 1986, after the draft finalized by the Rubber Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

0.2 This standard is the first in the new SR (synthetic rubber) series for common methods of test which are applicable to all types of synthetic rubbers currently indigenously produced, namely, styrene-butadiene rubber (SBR), acrylonitrile butadiene rubber (NBR) and polybutadiene rubber (BR). Other unified test methods similarly applicable to these synthetic rubbers will form the subsequent parts of this (SR) series.

0.3 Method of test for determination of antioxidants in styrene-butadiene rubber (SBR) had been originally covered in SBR : 6 of IS : 4518 (Part 1)-1967*. Later a method of test for determination of antioxidants in polybutadiene rubbers (BR) was issued as draft Indian Standard under document No. PCDC 14 (385). Methods of test for polybutadiene rubbers: Part 3 Determination of antioxidants.

0.3.1 While conceiving the idea of common methods of test for synthetic rubber under SR (synthetic rubber) series, the Committee took cognizance of the fact that the present methods for determination of antioxidants in SBR and BR could be unified and a method of test for determination of antioxidants in all types of synthetic rubbers evolved and published under SR series.

0.4 Determination of antioxidants is important as it provides information to the consumer which helps him in compounding techniques.

*Methods of tests for styrene-butadiene rubbers (SBR): Part 1 Determination o volatile matter, total ash, organic acid, soap, antioxidants, bound styrene and mooney viscosity.

0.5 In the preparation of this standard considerable assistance has been derived from ASTM D 1416-1983 Standard methods for rubber from synthetic sources—Chemical analysis, issued by American Society for Testing and Materials, USA.

0.6 For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS : 2-1960*. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard

1. SCOPE

1.1 This standard prescribes a method for the quantitative estimation of a known antioxidant (amine or phenolic) in synthetic rubber. The antioxidant should have a distinct UV absorption band.

2. QUALITY OF REAGENTS

2.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1977†) shall be employed in tests.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the result of analysis.

3. OUTLINE OF THE METHOD

3.1 A representative sample of the polymer is extracted into ethanol-toluene aziotrope (ETA) solvent. The absorbance of a diluted portion of the extract with or without further chemical treatment, is measured by an ultra-violet spectrophotometer, from which the antixoidant content is calculated.

4. APPARATUS

4.1 Spectrophotometer — A suitable UV spectrophotometer, with wavelength accurate to ± 0·1 nm and absorbance precision of ± 0·005, and capable of operating in the 200-400 nm region shall be used. The type of recorder to be used is optional.

4.2 Mechanical Shaker — Any wrist-action shaker.

4.3 Analytical Balance — Accuracy 0·000 1 g.

4.4 Volumetric Flasks — 50, 100, 250-ml into ground-glass stoppers.

4.5 Quartz-Cell — 1 cm cells (matching).

*Rules for rounding off numerical values (*revised*).

†Specification for water for general laboratory use (*second revision*).

5. REAGENTS

5.1 Spectroscopic Solvent — Methylcyclohexane and ethanol (*see* Table 1) having an optical transmission greater than 90 percent and toluene with transmission greater than 30 percent at the wavelength specified for the antioxidant to be determined.

TABLE 1 SOLVENTS AND TEST CONDITIONS FOR ANTIOXIDANT DETERMINATION

Antioxidant	Spectroscopic Solvent	Wavelength (nm)	Typical Background Correction per Gram of SBR per 250 ml	
			Hot Type	Cold Type
Phenylbetanaphthylamine (PBNA)	Toluene	309 ± 1	0·085	0·280
	Methylcyclohexane	309 ± 1	0·115	0·325
Acetone-diphenylamine condensation product (BLE)	85 percent methylcyclohexane and 15 percent ethanol*	288 ± 1	0·235	0·495
Mixed alkylated diphenylamines	85 percent methylcyclohexane and 15 percent ethanol	288 ± 1	0·225	0·495
		288 ± 1	0·235	0·495

*Use anhydrous ethanol.

5.2 Ethanol — Anhydrous grade.

5.3 Ethyl Alcohol-Toluene Azeotrope (ETA) — Mix 70 volumes of ethanol and 30 volumes of toluene; reflux for 4 hours over CaO and distil. Collect the distillate, discarding first and last fraction keeping only that distillate, coming over within a range of 1°C.

5.4 Alcoholic KOH — 14 g of potassium hydroxide (KOH) is ground with successive 50 ml portions of anhydrous ethanol till complete dissolution, then dilute to 400 ml and filter quickly. Keep in sealed dark bottles overnight before use.

NOTE — Needed when the antioxidant to be determined is mixed alkylated phenols.

5.5 Ethanol-Phenol (EP) Solution — Dissolve about 0·300 g of phenolic antioxidant in one litre of ethanol.

6. PROCEDURE

6.1 Prepare ETA extract following the procedure given below.

6.1.1 Take a portion of rubber at least 250 g prepared according to **3.1** of IS : 4518 (Part 1)-1967* and sheet it out on a laboratory mill by pressing it, not more than twice, between the cold rolls set at 0·25 mm distance. Weigh accurately two pieces of about 10 g of sheeted rubber. Place in an oven at 100° to 105°C for at least one hour and until the loss in weight on successive weighings at half-hour intervals is less than 1 mg. Pass through mill and get thin (less than 0·5 mm thick) sheet out. Cut the sheet into small strips of not wider than 10 mm and not longer than 50 mm.

6.1.2 Add 100 ml of ethanol-toluene azeotrope to the wide mouth flask. Accurately weigh 6 g of the strips. Add each strip of the weighed sample separately to the flask, swirling the flask after each addition so that each strip is thoroughly wetted with solvent. To prevent the strips from sticking to the flask, place a filter paper at the bottom of the flask. Use wire gauze or asbestos mat between the flask and the hot plate. Reflux the contents for one hour. Decant the liquid into the volumetric flask. Add a second 100-ml portion of the ETA to the rubber sample and reflux again for one hour. Decant liquid into the volumetric flask. Rinse the sample with successive 10 ml portions of fresh ETA and add these rinsings to the volumetric flask. Cool the ETA solution to room temperature and add enough fresh ETA to bring the volume to the 250-ml mark. Mix the contents thoroughly.

6.2 Method for Amine Antioxidants — Pipette accurately 2 ml of the ETA extract into a 100-ml volumetric flask, and make-up the 100 ml mark with spectroscopics solvent (*see* Table 1).

6.2.1 In case absorptivity (α) of the antioxidant is unknown, then determine α in the following manner and prepare a table for amine antioxidants for ready reference in future. (If α can be easily referred, the procedure in **6.2.1** can be eliminated.) Obtain two or more representative samples of the antioxidant which shall, in the case of acetone diphenylamine reaction product and mixed alkylated diphenylamines, be heated to a temperature at which they can easily flow. Thoroughly mix the antioxidant and prepare a standard solution of it in the proper spectroscopic solvent. The convenient strengths of the solutions are as follows:

a) Phenyl-β naphthylamine	0·24 g/l
b) Acetone — diphenylamine	0·24 g/l
c) Mixed alkylated diphenylamine	0·32 g/l

*Methods of test for styrene-butadiene rubbers (SBR): Part 1 Determination of volatile matter, total ash, organic acid, soap, antioxidant, bound styrene and mooney viscosity.

The strength (c) shall be accurate to $\pm$ 0·000 5 percent. Carefully measure three 3·00 ml aliquots (d) of this solution into 100-ml volumetric flasks and make up the volume with the spectroscopic solvents. Determine absorbance of the solutions at appropriate wavelength (λ) (*see* Table 1) into the pure solvent kept in the reference beam. Make several measurements on each diluted aliquot until a reproducible absorbance result (A_s) is obtained.

6.2.2 Measure the absorbance (A_t) of the test solutions in matched 1 cm cells at the specified wavelength λ, keeping mixed solvent in the reference beam. The mixed solvent is made by adding ETA and the spectroscopic solvent in the same ratio as that used in the solution containing the ETA extract of the rubber.

NOTE — For both **6.2.1** and **6.2.2**, the absorbance observed shall be between 0·4 and 1·0. If not, use a different aliquot of the ETA extract so as to bring the absorbance within the desired range, being sure to use the same proportion of ETA in the beam as in the sample.

6.3 Method for Phenolic Antioxidants (Alkylated and other Substituted Phenols, Phenolic Esters, etc)

NOTE — Spectrophotometric measurements shall be made preferably the same day as the standards and the test-sample extract is prepared.

6.3.1 Prepare basic and neutral solutions in six separate 50-ml volumetric flasks as in Table 2.

TABLE 2 VOLUME IN MILLILITRES OF VARIOUS SOLVENTS FOR MAKING UP 50-ml OF BASIC AND NEUTRAL SOLUTIONS

Sl No.	Solution	EP Solution	ETA Solvent	0·5 M KOH Solution	ETA Extract of Test Sample	Ethanol (to 50-ml Mark)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
i)	Basic standard(BS)	5	5	10	—	30
ii)	Basic reference(BR)	—	5	10	—	35
iii)	Basic test (BT)	—	—	10	5	35
iv)	Neutral standard(NS)	5	5	—	—	40
v)	Neutral reference(NR)	0	5	—	—	45
vi)	Neutral test (NT)	—	—	—	5	45

6.3.2 Using matched 1 cm cells, absorbance (A) of the solution are measured at 301 nm, keeping the corresponding reference solution in the reference beam.

NOTE — 301 nm should be used for mixed alkylated phenols antioxidant. For other phenols or phenolic esters, the quantities of standard material and of sample and the value of the wavelength are to be adjusted.

7. CALCULATION

7.1 For Amine Antioxidants

7.1.1 Calculate the absorptivity as follows:

$$\alpha = \frac{100\ A_S}{c\ d}$$

where

A_S = absorbance of standard solution,

c = concentration of the antioxidant in the standard as g/l; and

d = volume of aliquot in ml taken from the standard solution.

7.1.1.1 For SBR, correct the absorbance of a standard solution as follows:

A_S = [Observed A_S — backgroud correction factor]

7.1.2 Calculate the percentage antioxidant a follows:

$$\text{Amine antioxidant, percent by mass} = \frac{2\ 500\ A_t}{m\ V\ \alpha}$$

where

A_t = absorbance of solution,

V = volume (ml) of extract dissolved in spectroscopic solvent,

m = mass of rubber (g) of original sample extracted, and

α = absorptivity (*see* **7.1.1**).

7.2 For Phenolic Antioxidants

7.2.1 Calculate absorptivity difference ($\triangle_S$) as follows:

$$\text{Absorptivity difference } (\triangle_S) = \frac{A_{BS} - A_{NS}}{0{\cdot}030}$$

where

A_{BS} = absorbance of basic standard solution; and

A_{NS} = absorbance of neutral standard solution.

7.2.2 Calculate the percentage antioxidant as follows:

$$\text{Mixed alkylated phenolic antioxidant concentration, percent by mass} = \left[\frac{A_{BT} - A_{NT}}{\triangle_B} \times 2{\cdot}4 \right] \times 100$$

where

A_{BT} = absorbance of basic test solution,

A_{NT} = absorbance of neutral test solution, and

$\triangle_B$ = absorptivity difference (*see* **7.2.1**).

(*Continued from page* 2)

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